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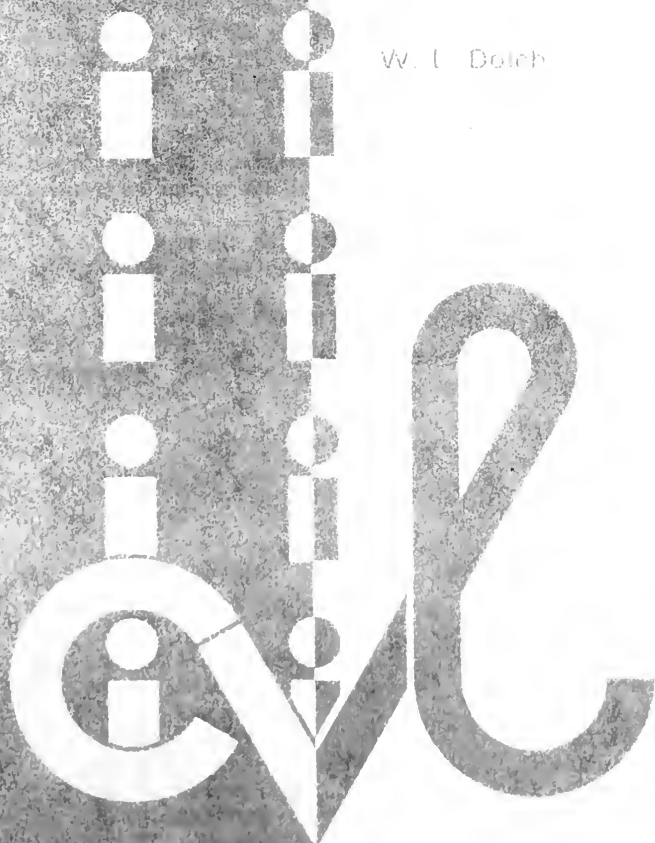


JOINT HIGHWAY RESEARCH PROJECT

FHWA/IN/JHRP-80/5

ANALYSIS OF HARDENED
CONCRETE FOR ADMIXTURE
CONTENT

W. L. Dolch



PURDUE UNIVERSITY
INDIANA STATE HIGHWAY COMMISSION

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Final Report

ANALYSIS OF HARDENED CONCRETE FOR ADMIXTURE CONTENT

TO: H. L. Michael, Director
Joint Highway Research Project

FROM: W. L. Dolch, Research Associate
Joint Highway Research Project

May 14, 1980

Project: C-36-65D

File: 5-15-4

The following Final Report is submitted on the JHRP research study entitled "Analysis of Hardened Concrete for Admixture Content". This report has been authored by W. L. Dolch.

An earlier Interim Report in 1978 by L. C. Muszynski and with the same title as this Report established a technique for the identification of organic admixtures present in hardened concrete by means of high pressure liquid chromatography (HPLC). Extension of the admixture from concrete was accomplished by use of a ternary azcetrope composed of 75 percent (by volume) of methylethyl ketone, 14 percent ethanol, and 11 percent water. Using HPLC conditions were found which provided a distinction among the various admixtures. With a LiChrosorb RP-18, 10 micron column operated in a reversal phase and a carrier solvent of 80 percent acetonitrile and 20 percent water by volume, HPLC use permitted qualitative identification of the admixture substances used. The amount of admixture used, however, was not determined.

The purpose of this last phase of the Study was to seek quantitative evaluation of the admixtures used. The purpose was not fulfilled.

This is the Final Report on this research project and it is submitted to ISHC and FHWA for review and acceptance as fulfillment of the objectives of the Study.

Respectfully submitted,

W. L. Dolch/ms

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by
W. L. Dolch

Joint Highway Research Project

Project No.: C-36-65D

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Prepared as Part of an Investigation

Conducted by

Joint Highway Research Project
Engineering Experiment Station
Purdue University

in cooperation with the

Indiana State Highway Commission

and the

U.S. Department of Transportation
Federal Highway Administration

The contents of this report reflect the views of the author who is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Federal Highway Administration. This report does not constitute a standard, specification, or regulation.

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16. Abstract <p>An earlier Interim Report in 1978 by L. C. Muszynski and with the same title as this Report established a technique for the identification of organic admixtures present in hardened concrete by means of high pressure liquid chromatography (HPLC). Extension of the admixture from concrete was accomplished by use of a ternary azcotrop composed of 75 percent (by volume) of methylethyl ketone, 14 percent ethanol, and 11 percent water. Using HPLC conditions were found which provided a distinction among the various admixtures. With a LiChrosorb RP-18, 10 micron column operated in a reversal phase and a carrier solvent of 80 percent acetonitrile and 20 percent water by volume, HPLC use permitted qualitative identification of the admixture substances used. The amount of admixture used, however, was not determined.</p> <p>The purpose of this last phase of the Study was to seek quantitative evaluation of the admixtures used. The purpose was not fulfilled.</p>			
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INTRODUCTION

The work described here was a supplement to the larger study, previously reported in "Analysis of Hardened Concrete for Admixture Content" by L. C. Muszynski, 1978. This study was to determine the applicability of the technique that was earlier established to the problem of the quantitative determination of the admixture content in hardened concrete. The earlier study was concerned exclusively with the qualitative identification of these substances.

The previous study established the technique for the identification of the organic admixtures present in hardened concrete by means of high pressure liquid chromatography (HPLC). Two chief problems were addressed. The first was that of extraction of the admixture from the concrete. This was accomplished by the use of a ternary azeotrope composed of 75 percent (by volume) of methylethyl ketone, 14 percent ethanol, and 11 percent water, which boils at 73.2 C. The reasons for this choice were to obtain a constant boiling azeotrope that would lend itself to the Soxhlet extraction process, and the use of solvents of varying polarity and hydrogen donor-acceptor characteristics so as to have the widest possible solvent action for a variety of extractable substances. It was found that this solvent, when used in the Soxhlet technique, did extract the wide variety of admixtures tested.

The other problem was the discovery of the HPLC experimental conditions that would provide a distinction among the various admixtures

so they could be identified after extraction. The chief experimental conditions of concern were the best type of chromatographic column and the proper carrier solvent. After a large number of trials involving various kinds of experimental techniques, the column selected was a LiChrosorb RP-18, 10-micron column operated in reverse phase. The carrier solvent was a mixture of 80 percent acetonitrile and 20 percent water, by volume. The chromatograph was a Waters ALC/GPC 201 using both a Waters R-401 differential refractometer detector and a Waters 440 ultraviolet absorbance detector operating at 254 nm. This technique was used to analyze twenty different common admixtures extracted from hardened cement pastes that had been mixed at admixture/cement ratios recommended by the admixture manufacturers. Apparently successful separations were obtained, which permitted qualitative identification of these substances. It was, however, found that seemingly small details of apparatus, technique, and materials seemed to make disproportionate differences in the patterns obtained. It was emphasized that unknowns should be analyzed by comparison with companion control samples that had been run in exactly the same manner with respect to all details. See the complete report for many other details (Muszynski 1978).

The quantification of liquid chromatography has been discussed in many standard references (see for example, Snyder and Kirkland, 1974). The attempt made here consisted of running standards made by mixing one, two, and three times the recommended amounts of several common admixtures in cement pastes, extracting the admixtures from the hardened pastes, and comparing the resulting patterns.

for safety's sake. At first 17 hours was used; later it was changed to 21.

All details of evaporation of the extraction solvent, resolution in the carrier solvent, and chromatographic examination were exactly those used earlier. The only difference was an occasional change in the ultraviolet sensitivity setting, either for convenience or necessitated by slow decline in the photo cell sensitivity. Such a change alters the peak height, but neither peak form nor retention time.

Midway in the study it was necessary to replace the column. Still later the sample injector apparatus was replaced. What changes in the results may have been caused by the replacements are unknown, but may have been significant.

The results are shown in the appended figures.

DISCUSSION

The earlier work showed the UV spectrophotometer output to be more informative than that from the differential refractometer. Its superiority was due mainly to its much greater sensitivity. Obviously, it fails for materials that do not absorb at the frequency of operation. The equipment used here permitted detection at only one frequency (254 nm); more modern detectors that employ several (or many) frequencies are superior. A five-fold repetition of injections of one extract (Admixture M) showed UV output recorder traces that were identical, showing the absence of "short time" variability in the response of the equipment.

Three relatively early runs on Admixture G are shown in Figures 1, 2, and 3 for 1x, 2x, and 3x concentrations respectively. The blank is shown in Figure 4. In all these figures time runs from left to right, and the single vertical stroke is the time of injection of the sample into the chromatograph. The upper trace is the output of the refractometer, and the lower is that of the UV spectrophotometer. The zero times of the two traces are offset to avoid pen interference.

Major peaks exist at retention times (on the abscissa) of 1.8 and 2.7 scale divisions (cm). Perhaps unfortunately, the blank also contains peaks at these same positions. Peak areas were calculated for these two positions by the peak height times peak width at half-height technique. The units are cm. in., since the major divisions

on the abscissa are cm and those on the ordinate of the recorder paper are inches. The results are shown in Table 1, along with the areas of the knowns corrected by subtraction of the peak areas shown by the blank.

These results show a reasonable correlation for the 1.8 cm peaks; that is, the area differences between equal concentration increments are roughly equal. The same is not true for the 2.7 cm peak; those for 2x and 3x concentrations are almost the same. The good results for the 1.8 cm peak may be fortuitous, because it is probably risky to use for analytical purposes any peak that occurs in the blank, as do both of these shown. There is evidence that the peaks in the blank may come from non-volatile residues in the extraction solvent as well as from organic materials, such as grinding aids, in the cement. If this is so, and it probably is, then a blank run provides an uncertain correction factor, and probably only peaks that don't appear in the blank should be used for analytical purposes.

Some results for Admixture C are shown in Figures 5, 6, and 7, for 1x, 2x, and 3x dosages, respectively. The characteristic peaks are at 2.1 and 2.7 cm. The heights of the 2.1 cm peaks are about the same for the 2x and 3x samples. That of the 2.7 cm peak is smaller for the 3x than for the 2x. These results hardly support the validity of this as a quantitative method.

It will be noted that the pattern is different from that for Admixture G (Figures 1, 2, 3). Whether or not these patterns (for Admixtures C and G) resemble those found in the earlier study may be a matter of taste or interpretation of distinctions. There is a

general resemblance, but not a detailed one. These differences probably result from the aforementioned sensitivity of the results to instrumental and materials differences, and may only emphasize the importance of using a proper standard sample along with an unknown.

After these somewhat ambiguous results, considerable effort was spent on trying to refine the method, in terms mostly of changes in the extraction and carrier solvents. Unfortunately, no improvement was obtained.

After the injection system was replaced, all four admixture samples were re-run, beginning with the extractions. The extraction time was extended to 21 hours. The blank for this series is shown in Figure 8. It will be noted that its pattern is not the same as that of Figure 4, although the original paste sample was the same. No explanation for the difference is obvious, other than the aforementioned instrumental and materials variables.

The results for Admixture C are shown in Figures 9-11. The results again are not quantitative; the results for the 3x sample are obviously not 1.5 times those for the 2x, even if one discounts the 5.2 cm peak because it is in the same position as one for the blank. The only principal peak not in the blank is at 4.2 cm, and its size is not quantitatively related to the amounts of admixtures in the samples.

The results for Admixture G are shown in Figures 12-14. Although the patterns have a rough quantitative relationship to the amounts of admixture present, the details are disappointing. The areas of the 5.2 cm peaks are 2.7, 4.3, and 5.3 cm. in. for the 1x,

2x, and 3x concentrations. The only non-blank peak is at 4.2 cm; those areas for the three concentrations are 0.6, 0.9, and 0.8 cm. in., which is worse. Figure 15 shows a sample of this admixture from the earlier study that was run as a companion to the others. It will be noted that its pattern is almost identical to that in Figure 12, except for the long-time peaks.

The results for Admixture M are shown in Figures 16-18. The same remarks apply here that were used to describe the former two. Indeed, the pattern for the 1x concentration is the largest of the three.

The results for Admixture K are shown in Figures 19-21. The pattern for the 3x concentration is not even recognizable as the same as the other two; the 5.2 cm peak, prominent in the 1x and 2x concentration results is almost absent in Figure 21, except as a low shoulder. The areas for the 4.6 cm peaks show no better agreement.

A further, and very disturbing, feature of this last series of results is their close resemblance to each other (although fine details vary) and their considerable difference from the results for corresponding samples in the earlier study.

Altogether, the only conclusion that can be drawn from these results is that the presently-used HPLC technique is not appropriate for the quantitative estimation of organic admixtures in hardened concrete.

ACKNOWLEDGEMENTS

The able assistance of Mrs. Janet Lovell is gratefully acknowledged. The work was financed by The Federal Highway Administration and The Indiana State Highway Department. This support is appreciated.

REFERENCES

Muszynski, L. C., "Analysis of Hardened Concrete for Admixture Content", Thesis, Purdue University, 1978.

Snyder, L. R. and Kirkland, J. J., "Introduction to Modern Liquid Chromatography", Chap. 13, Wiley, 1974.

TABLE I

Admixture G

Concentration	Retention Time, cm.	Peak Area, cm. in.	Corrected Peak Area, cm. in.
1x	1.8	1.07	0.44
2x	1.8	1.40	0.77
3x	1.8	1.75	1.12
1x	2.7	2.89	0.62
2x	2.7	3.56	1.29
3x	2.7	3.58	1.31
Blank	1.8	0.63	--
Blank	2.7	2.27	--

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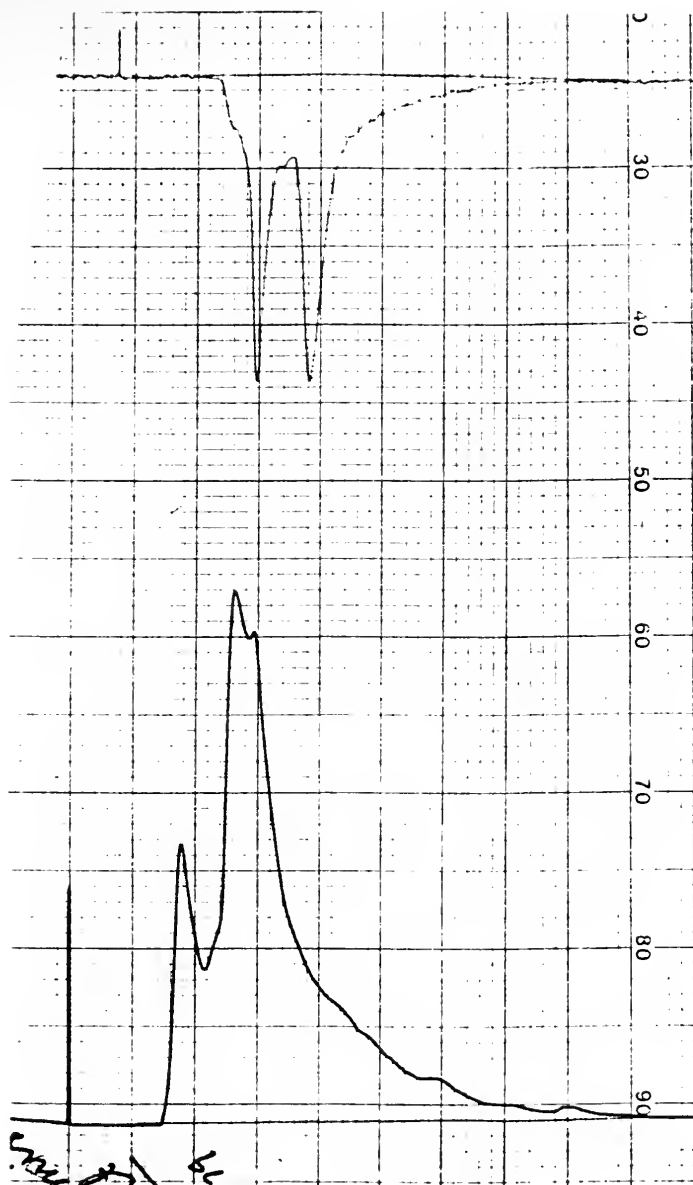


Fig. 1. Admixture G, 1X concentration.



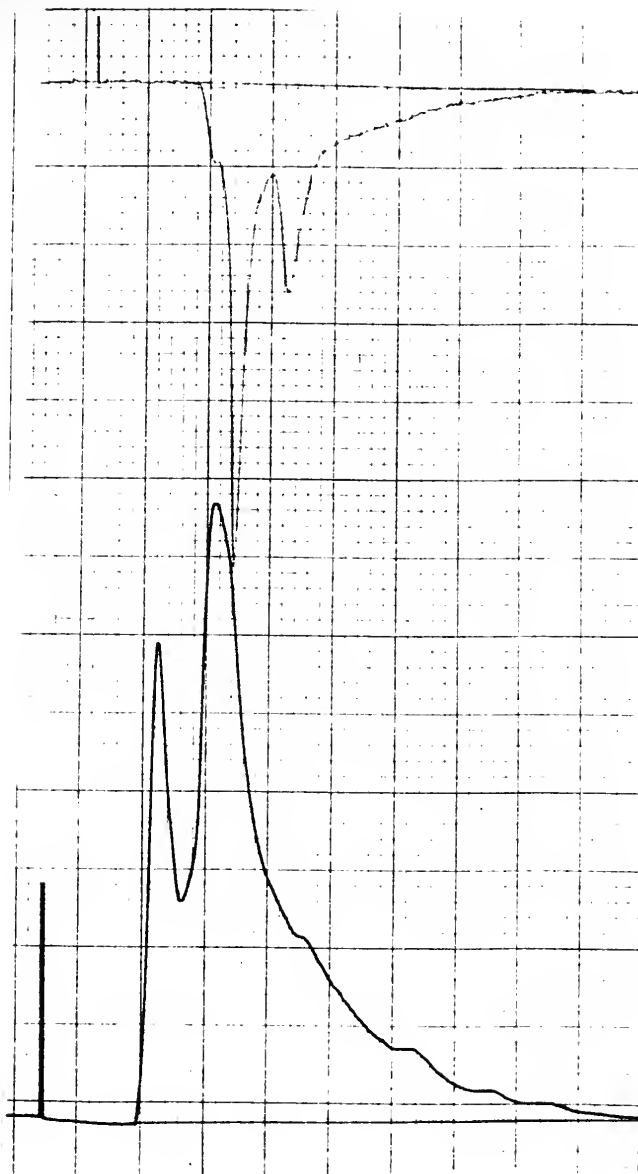


Fig. 2. Admixture G, 2X concentration.



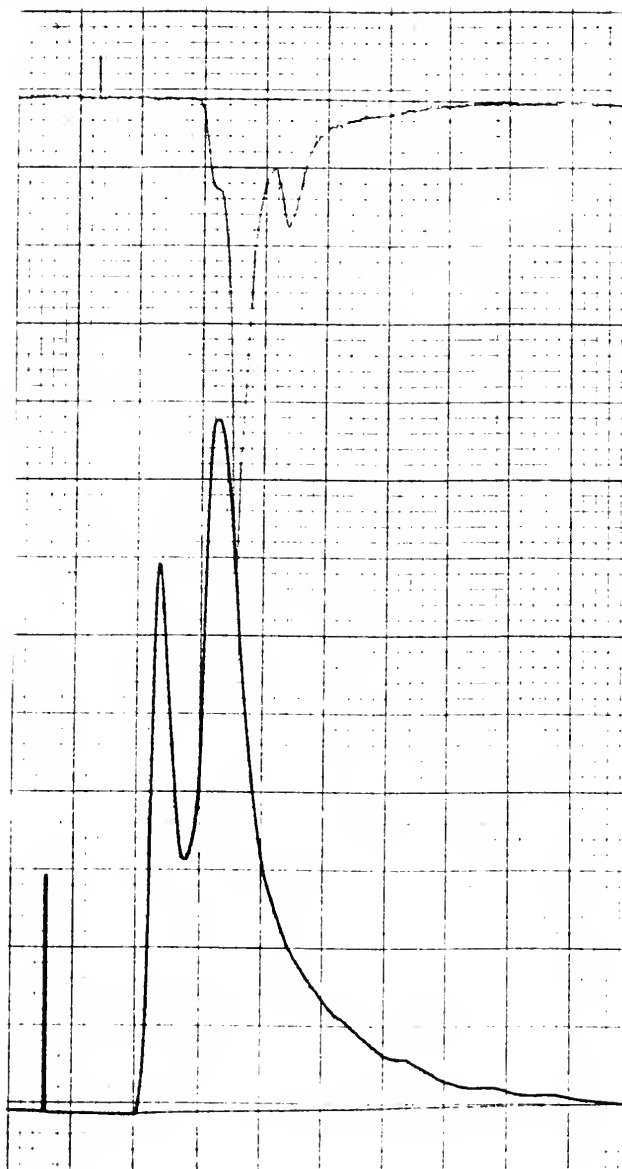


Fig. 3. Admixture G, 3X concentration.

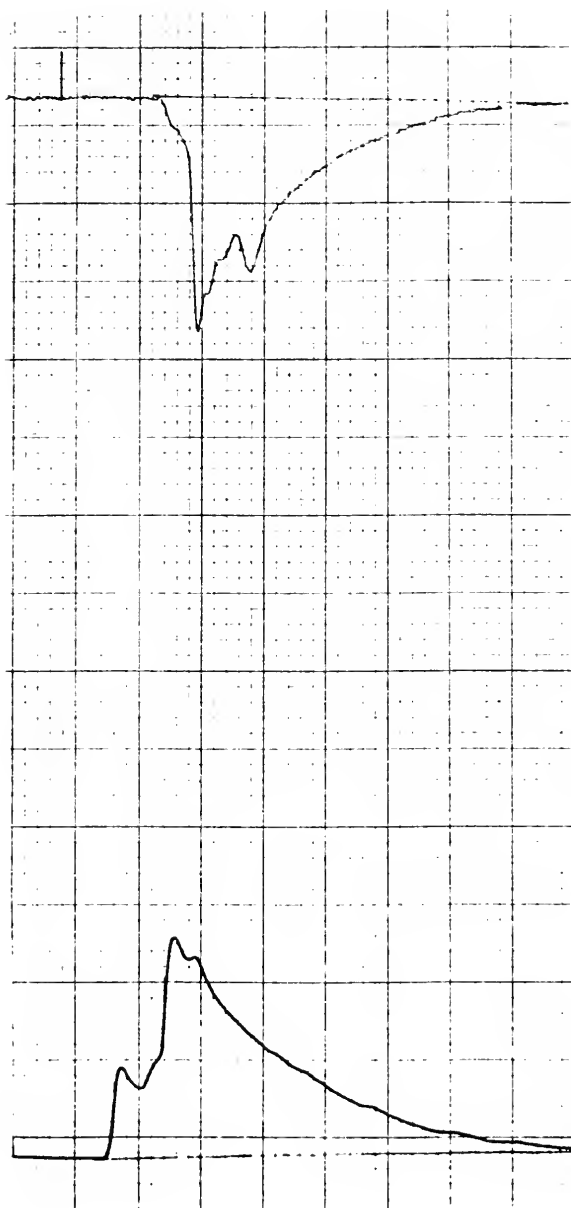


Fig. 4. Blank, no admixture.

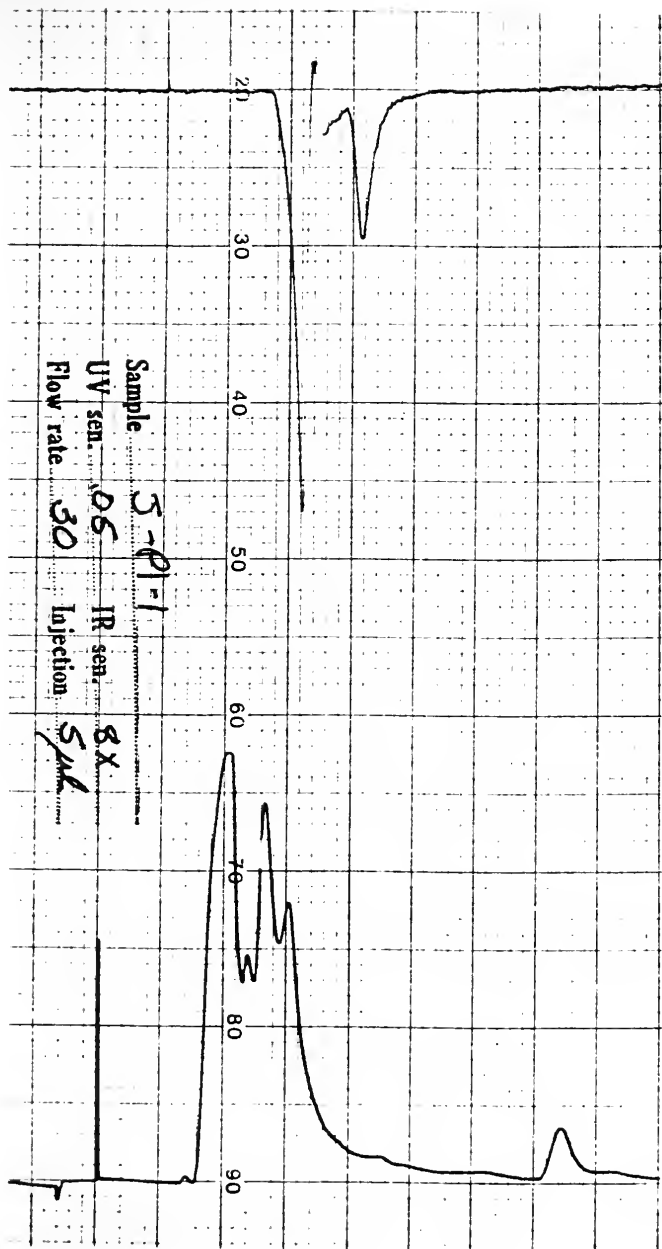


Fig. 5. Admixture C, 1X concentration.

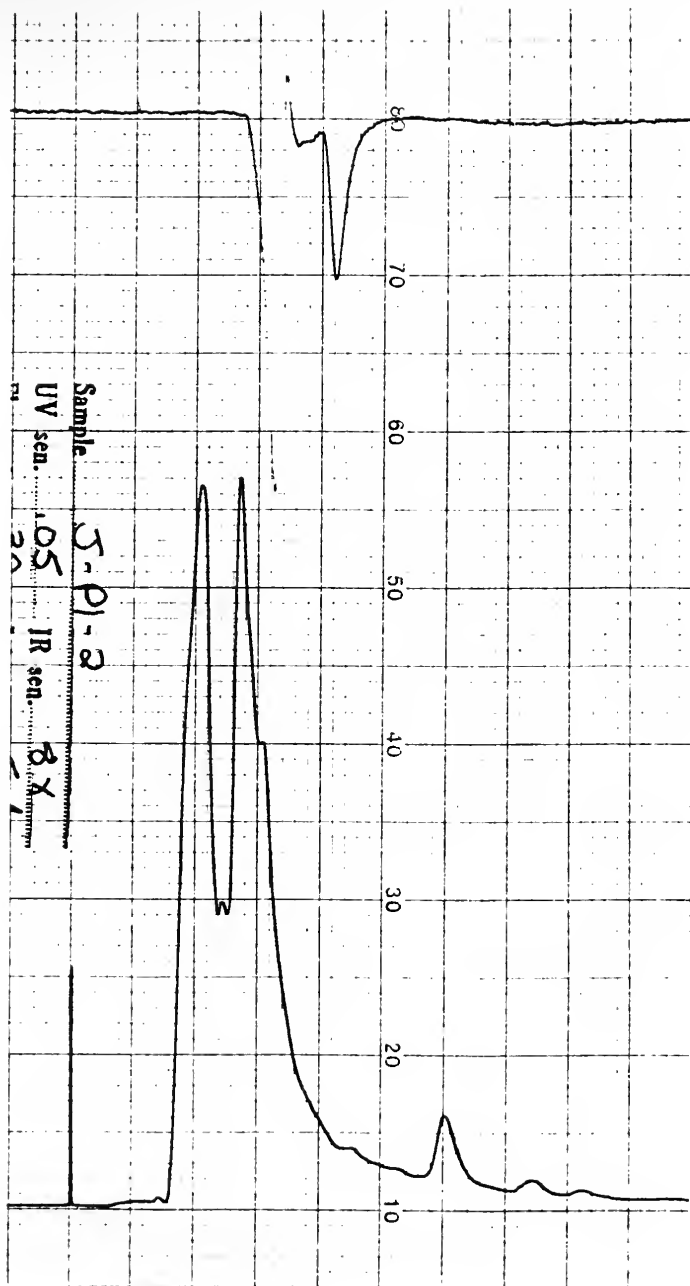


Fig. 6. Admixture C, 2X concentration.

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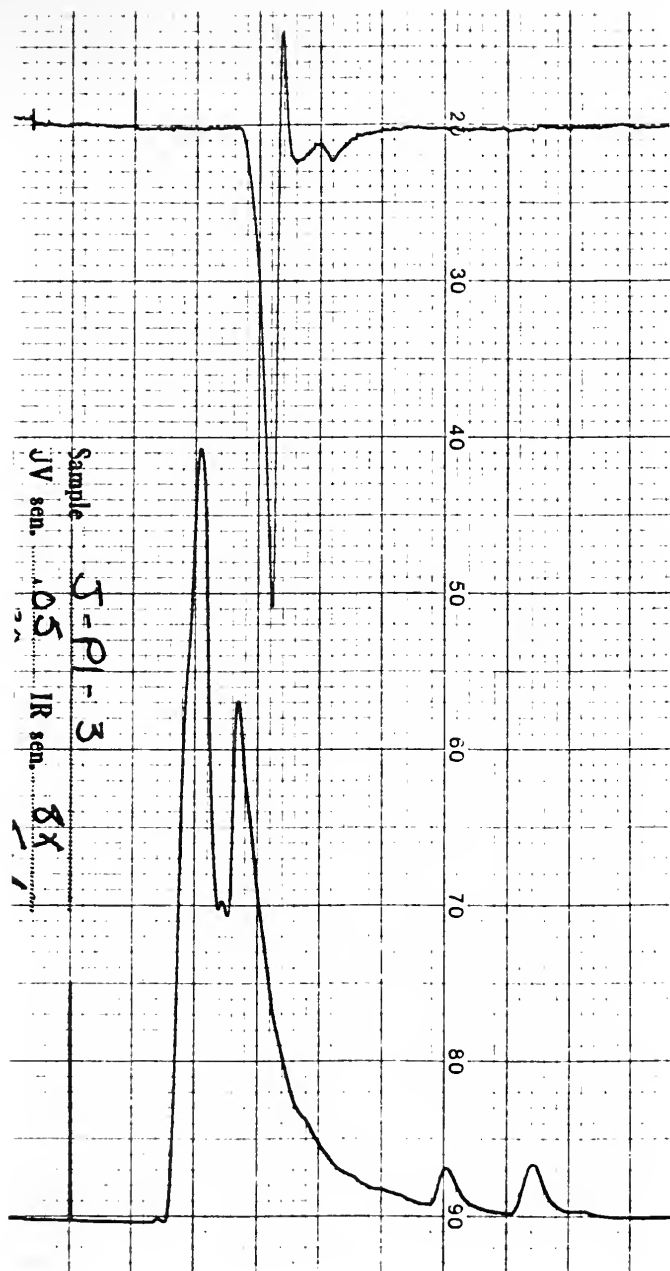


Fig. 7. Admixture C, 3X concentration.

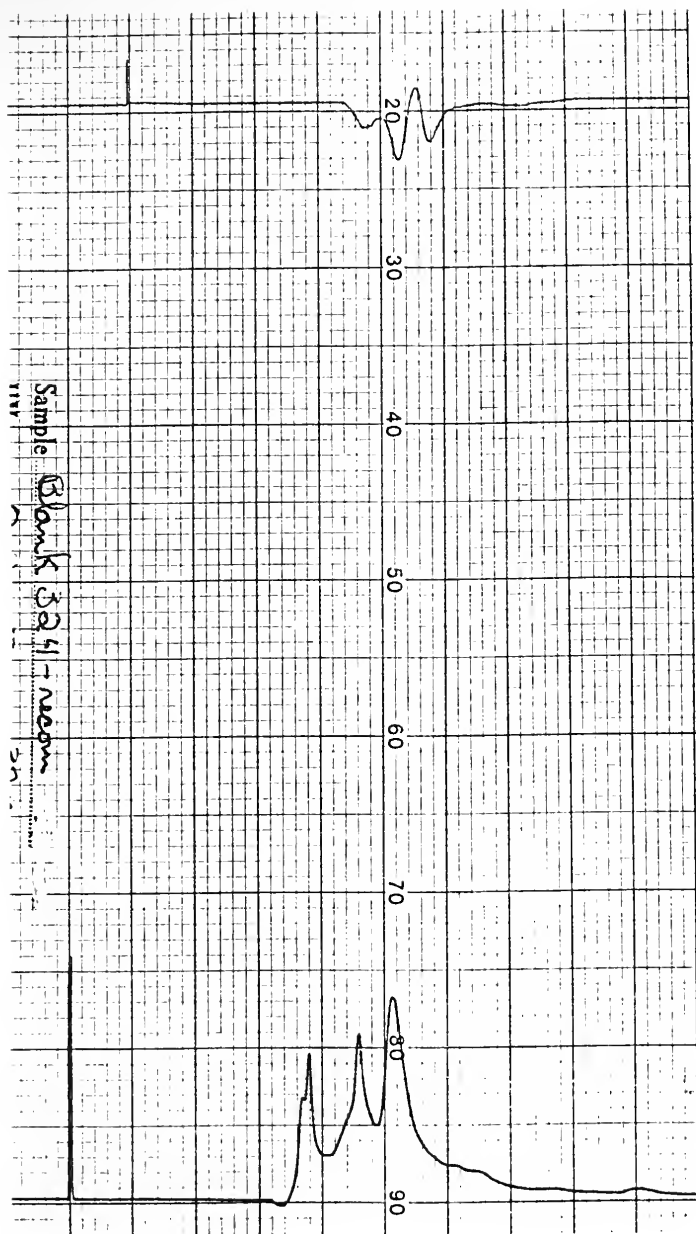


Fig. 8. Blank, no admixture.

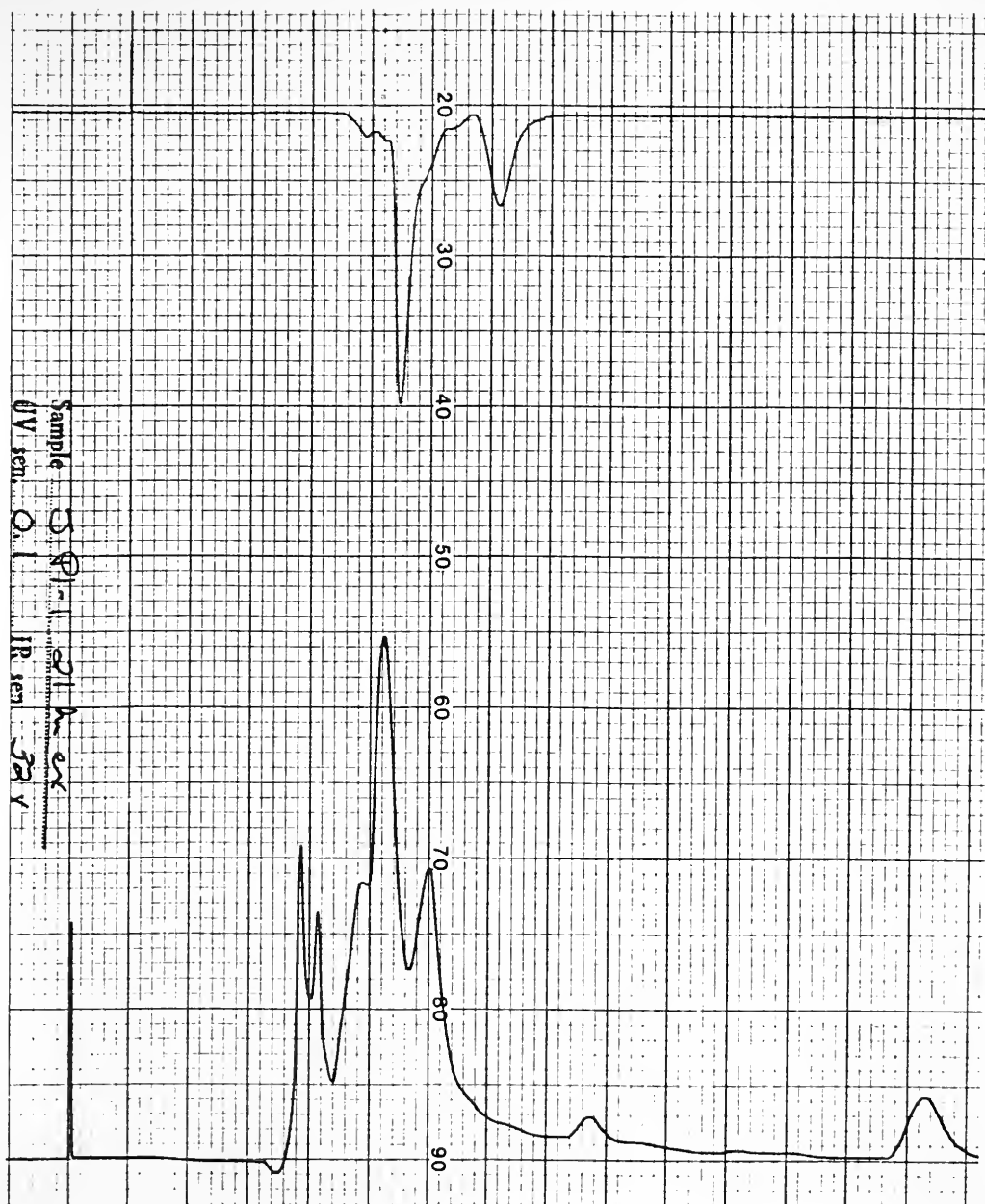


Fig. 9. Admixture C, 1X concentration.

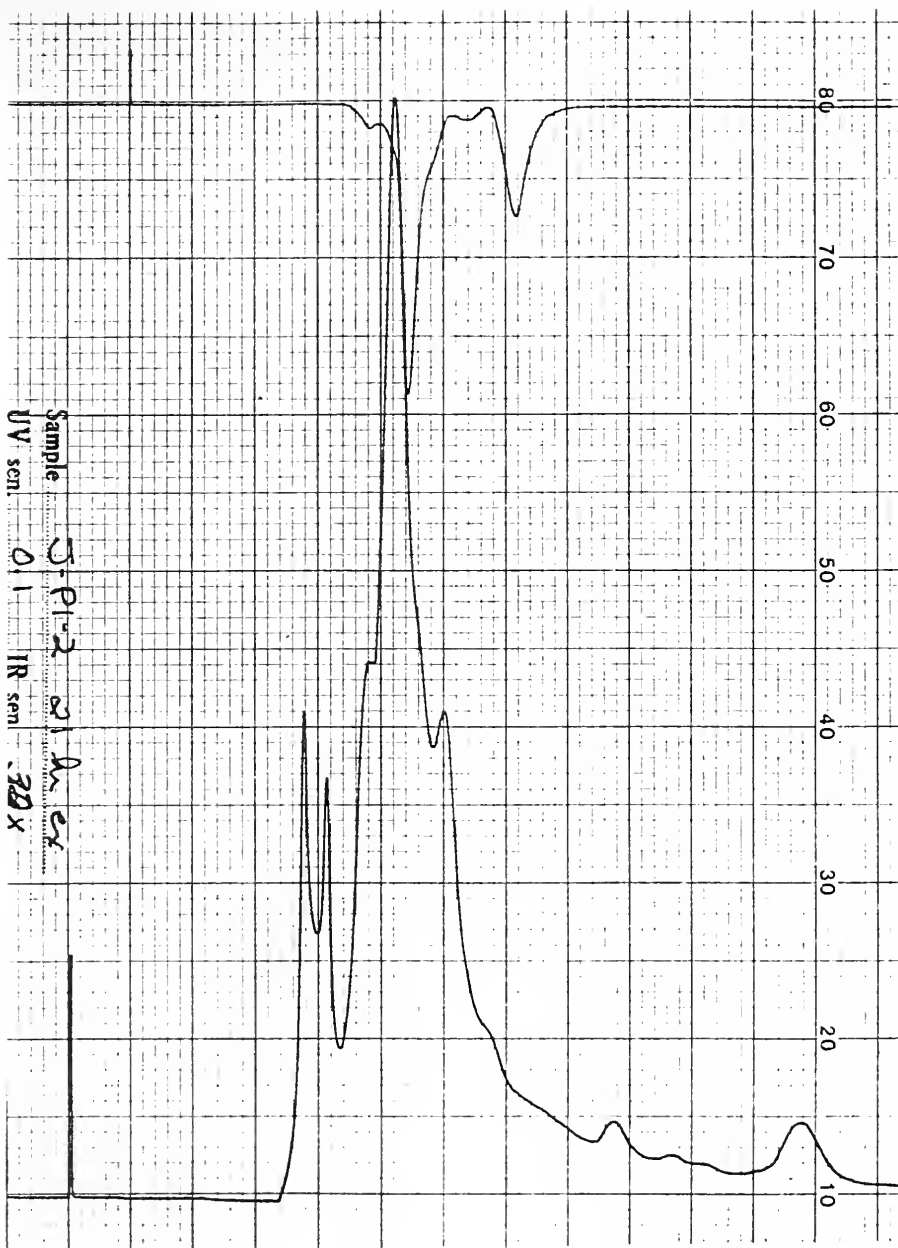


Fig. 10. Admixture C, 2X concentration.

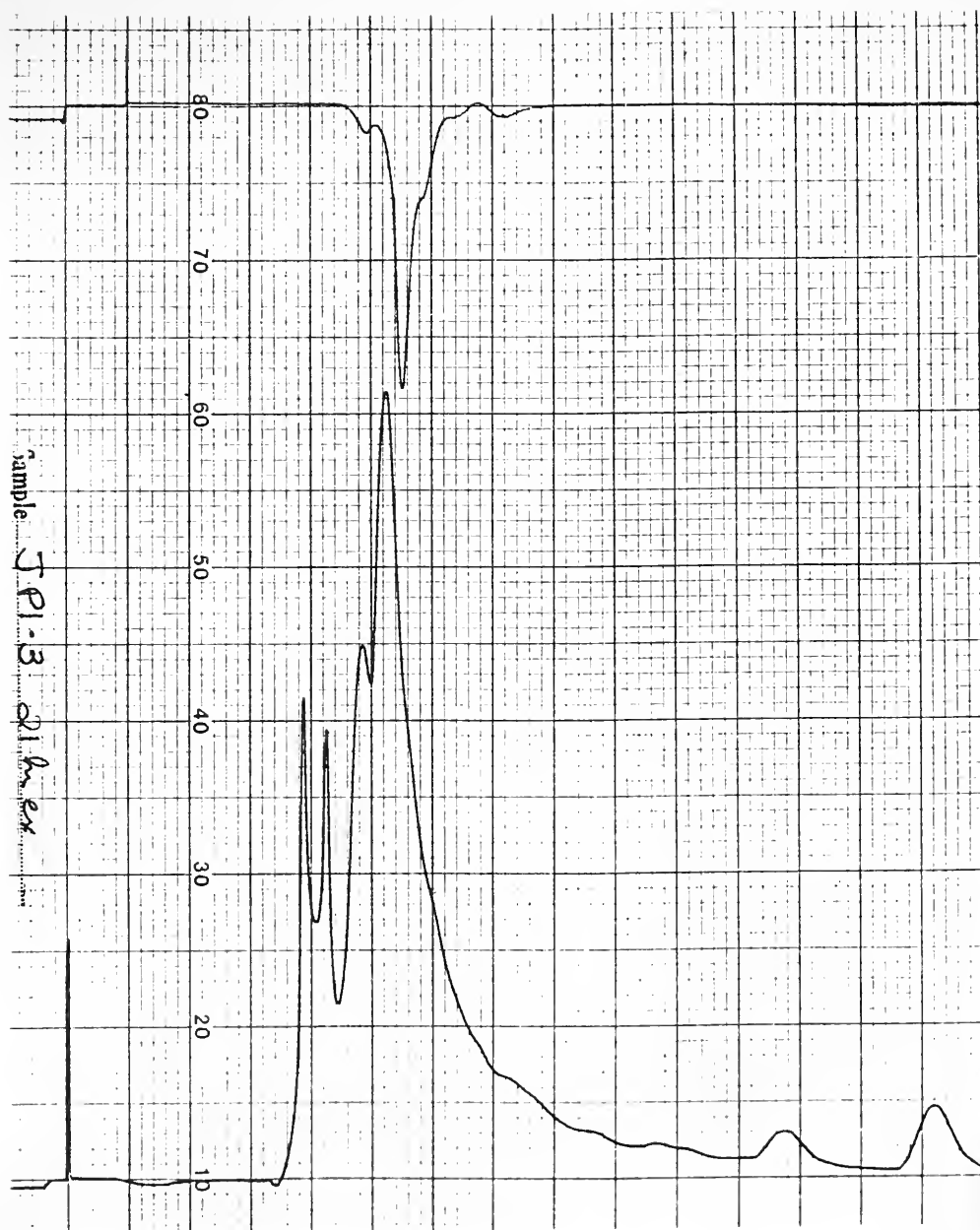


Fig. 11. Admixture C, 3X concentration.

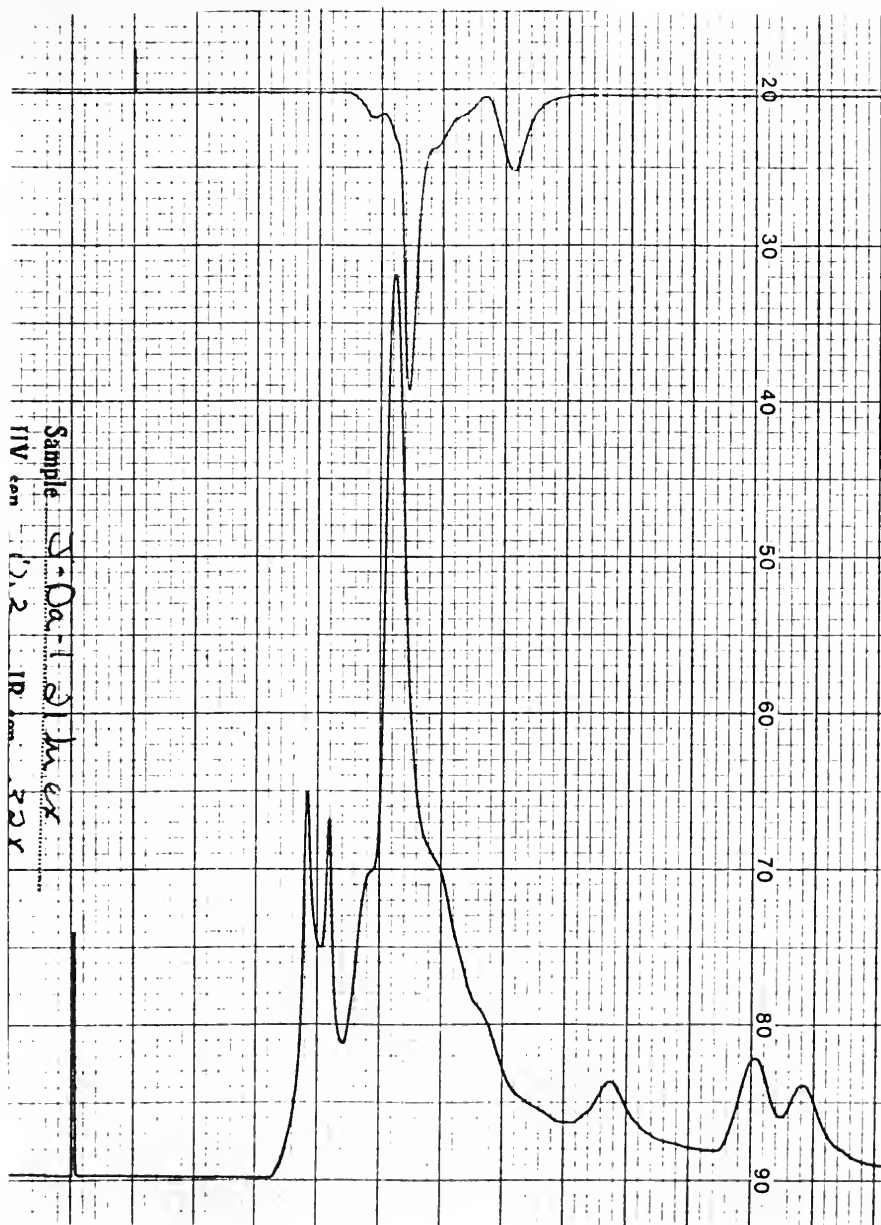


Fig. 12. Admixture G, 1X concentration.

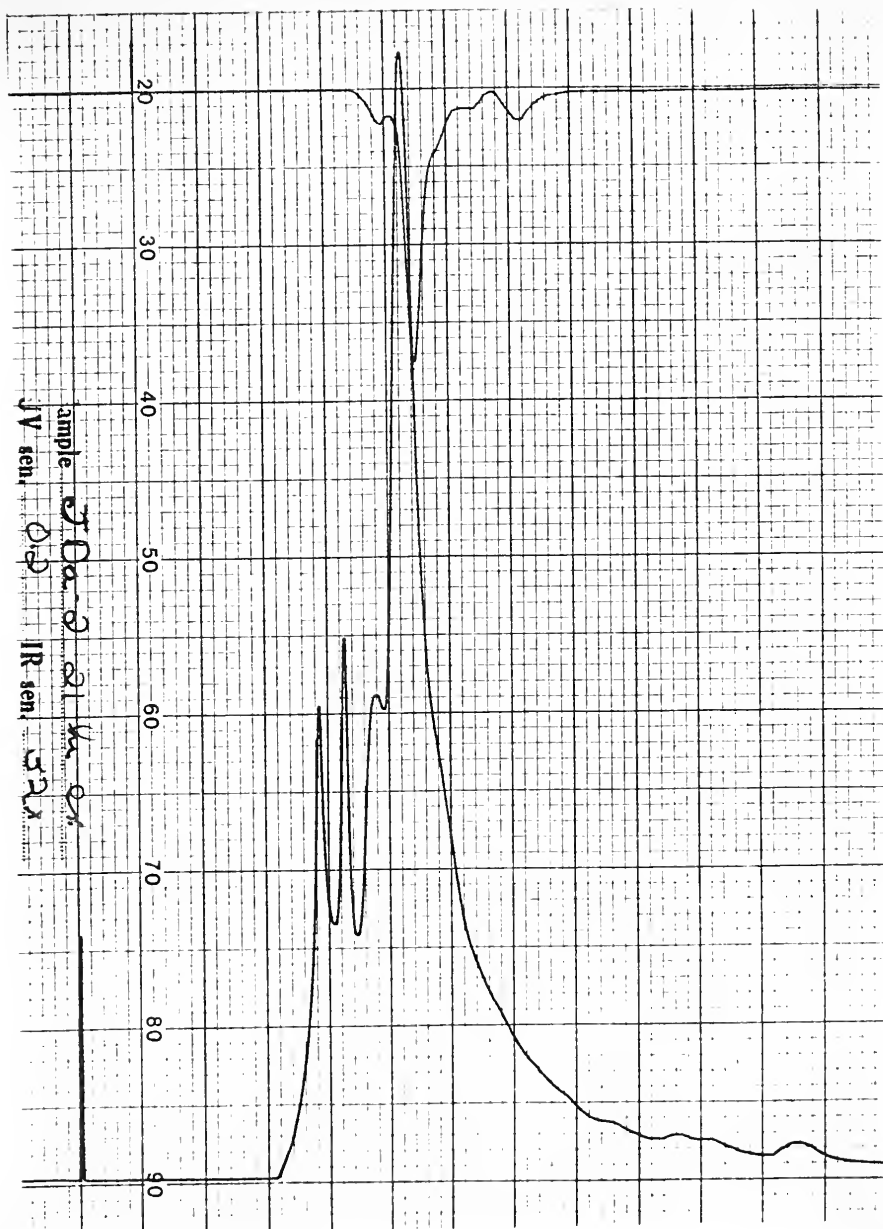


Fig. 13. Admixture G, 2X concentration.

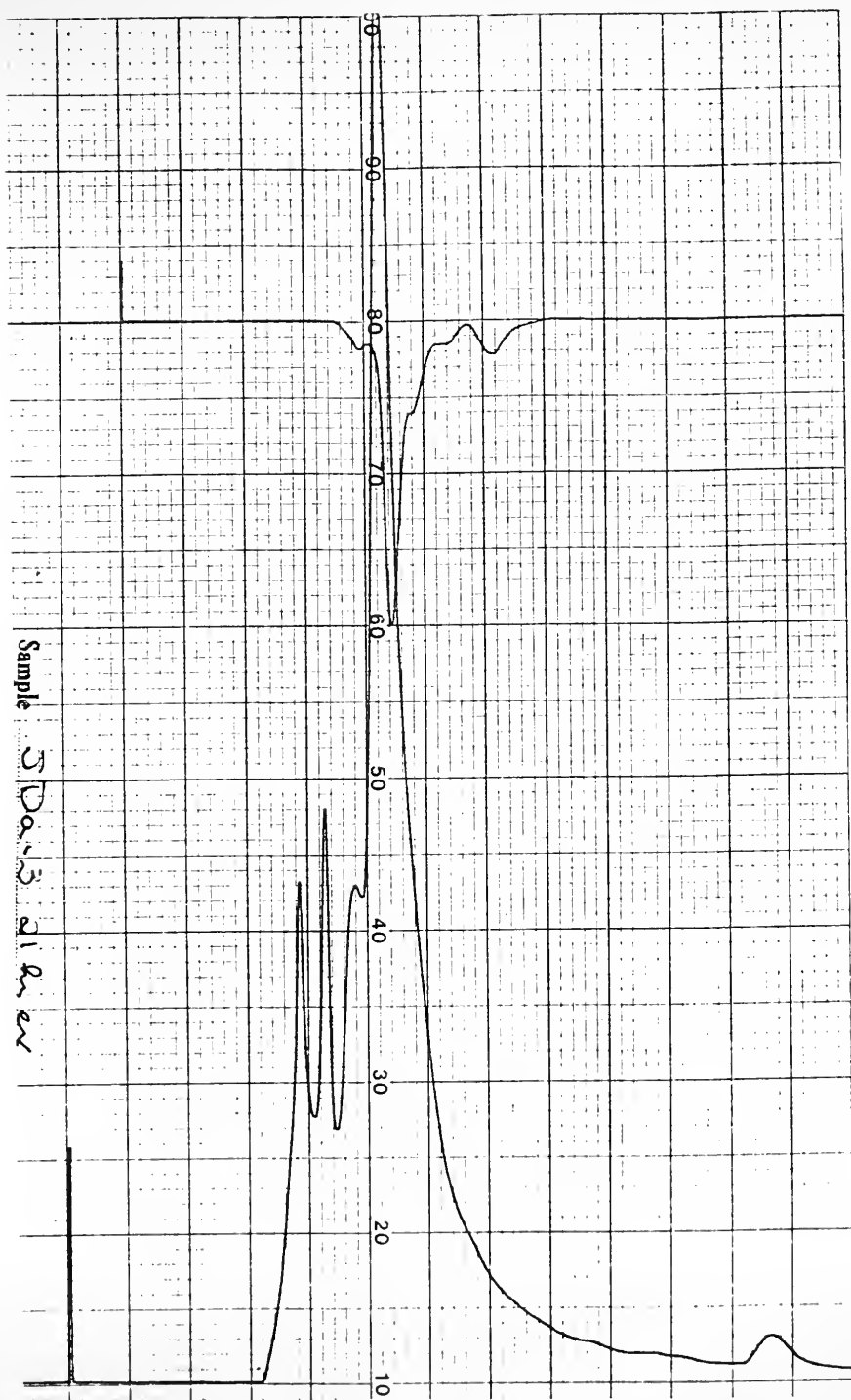


Fig. 14. Admixture G, 3X concentration.

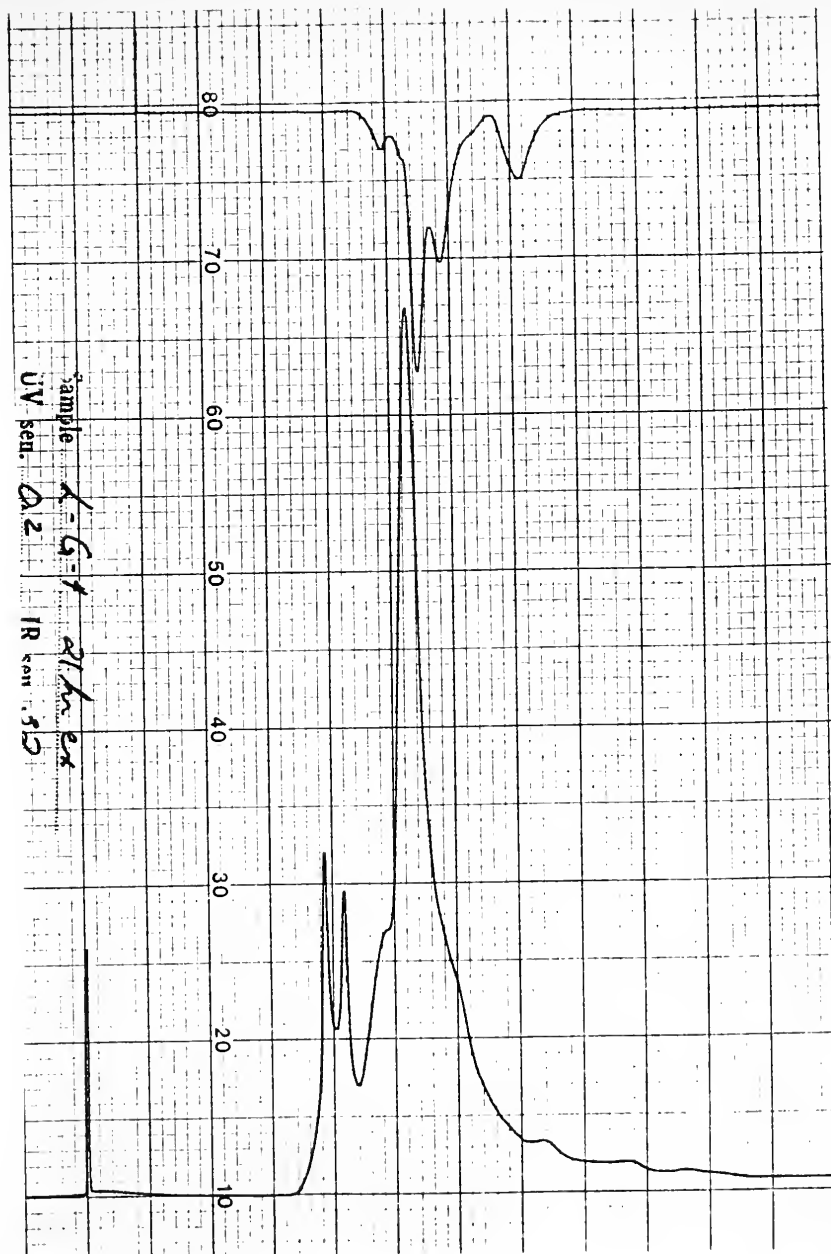


Fig. 15. Admixture G, 1X concentration, sample from earlier study (Muszynski 1978).

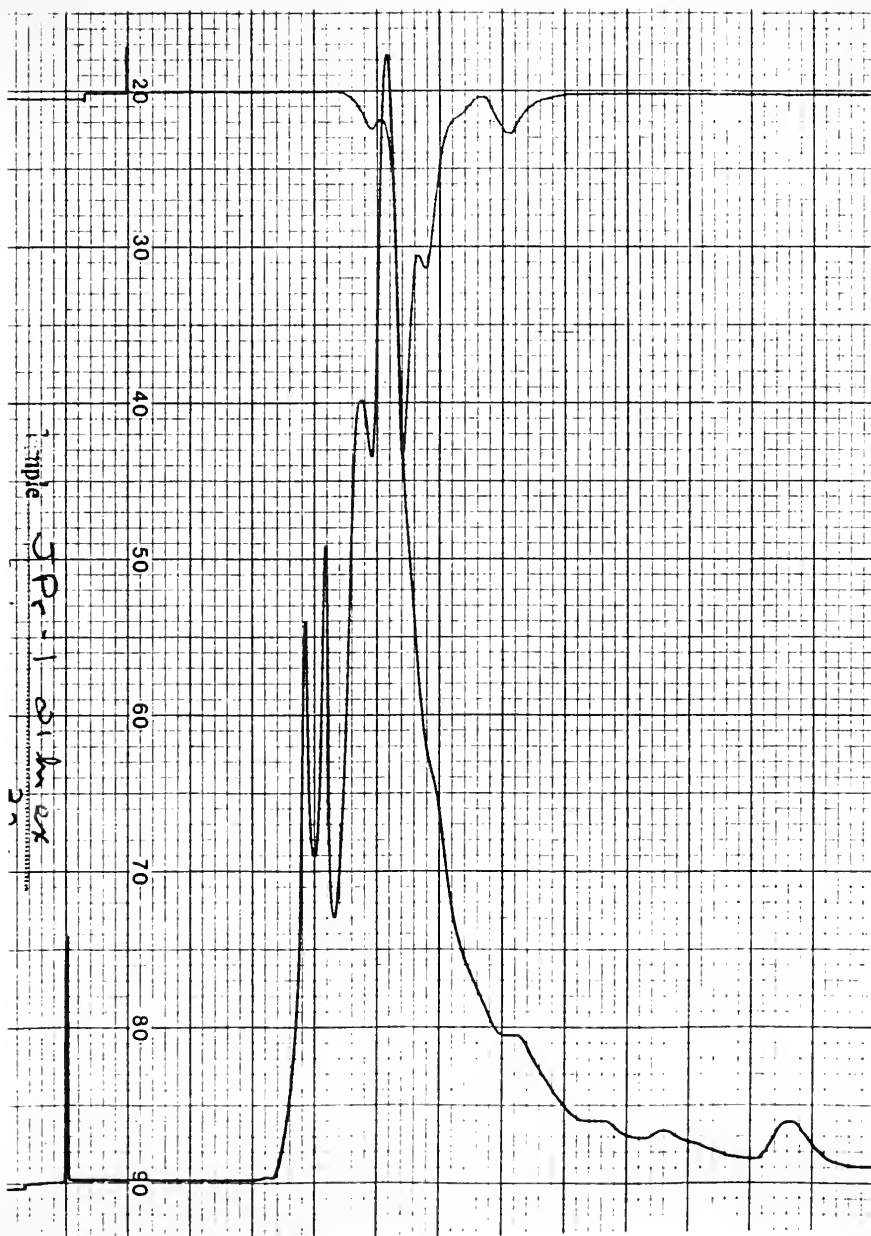


Fig. 16. Admixture M, 1X concentration.

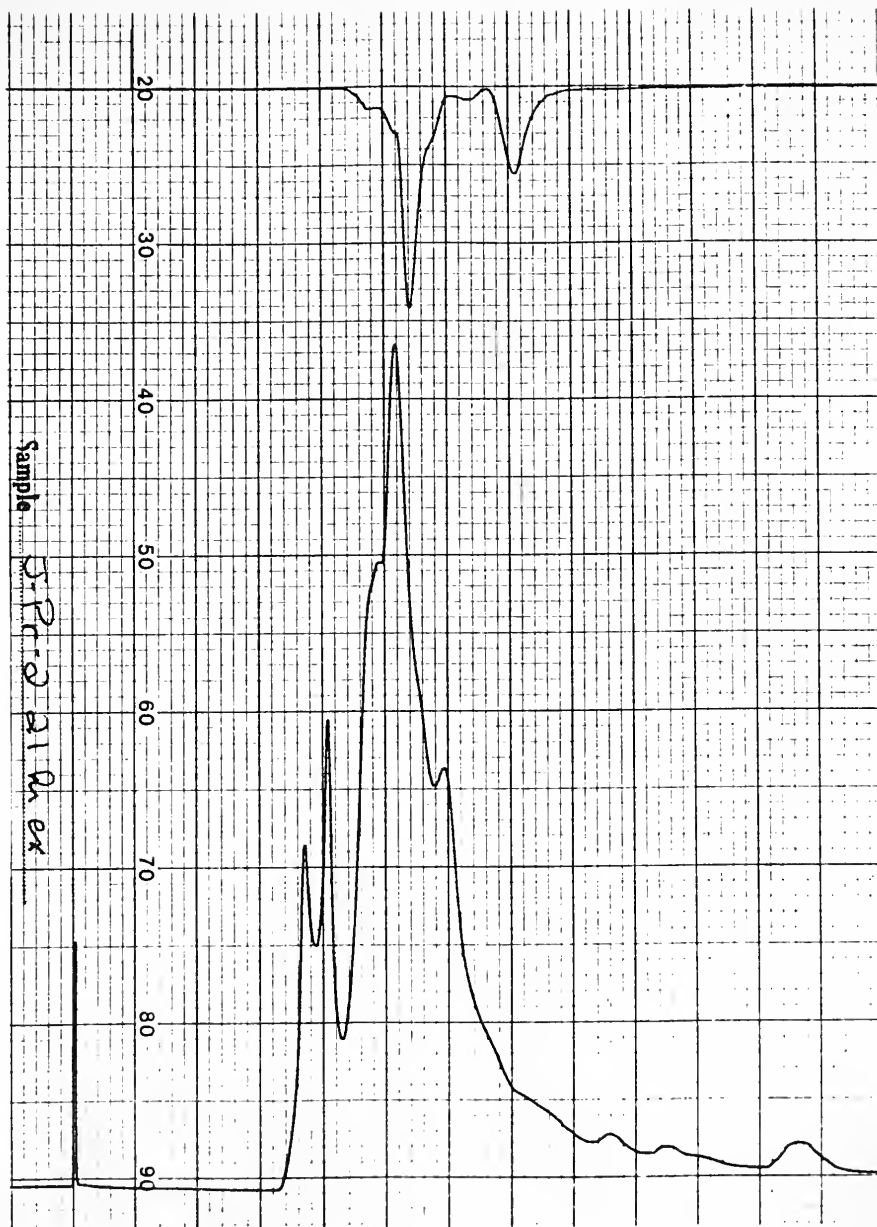


Fig. 17. Admixture M, 2X concentration.

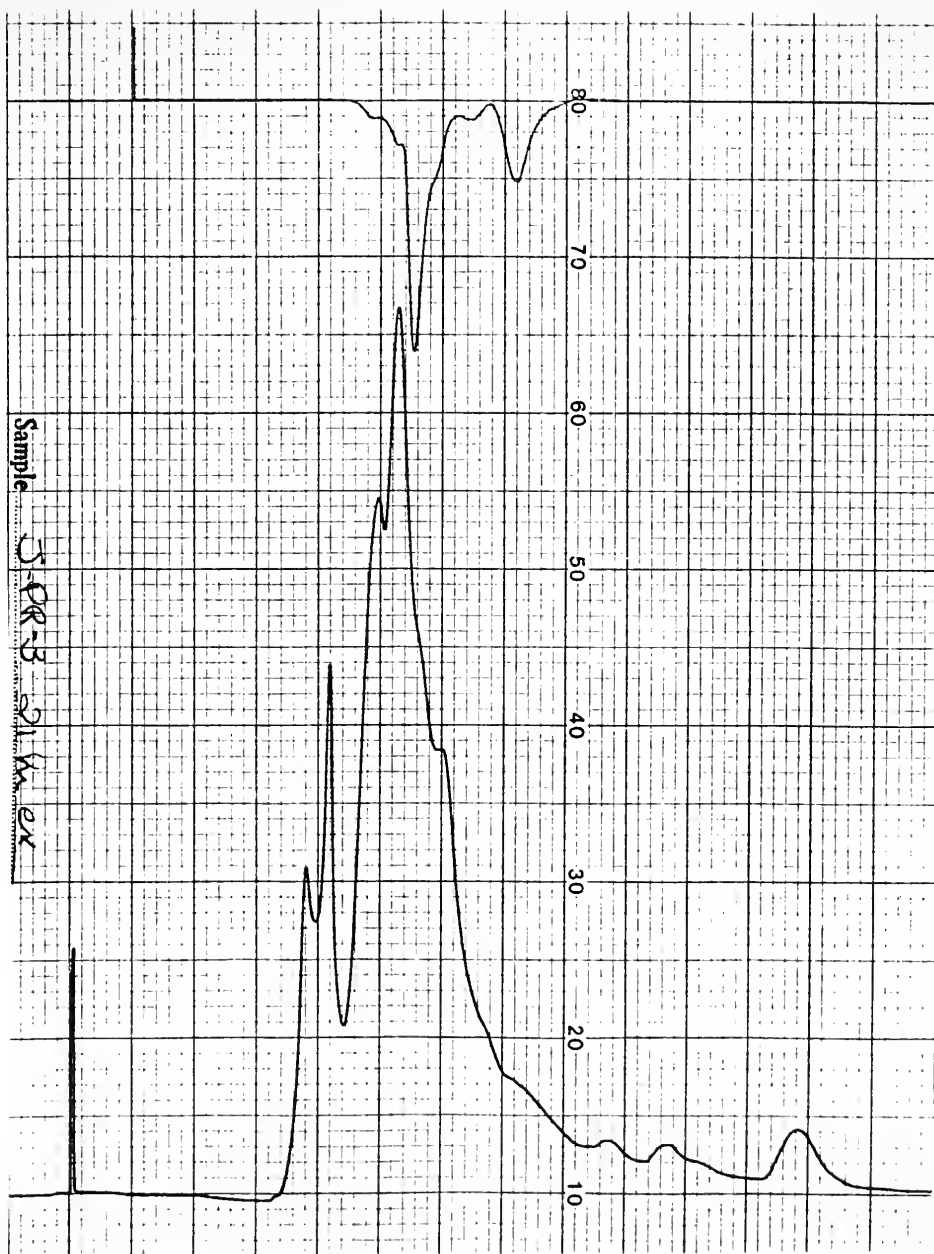


Fig. 18. Admixture M, 3X concentration.



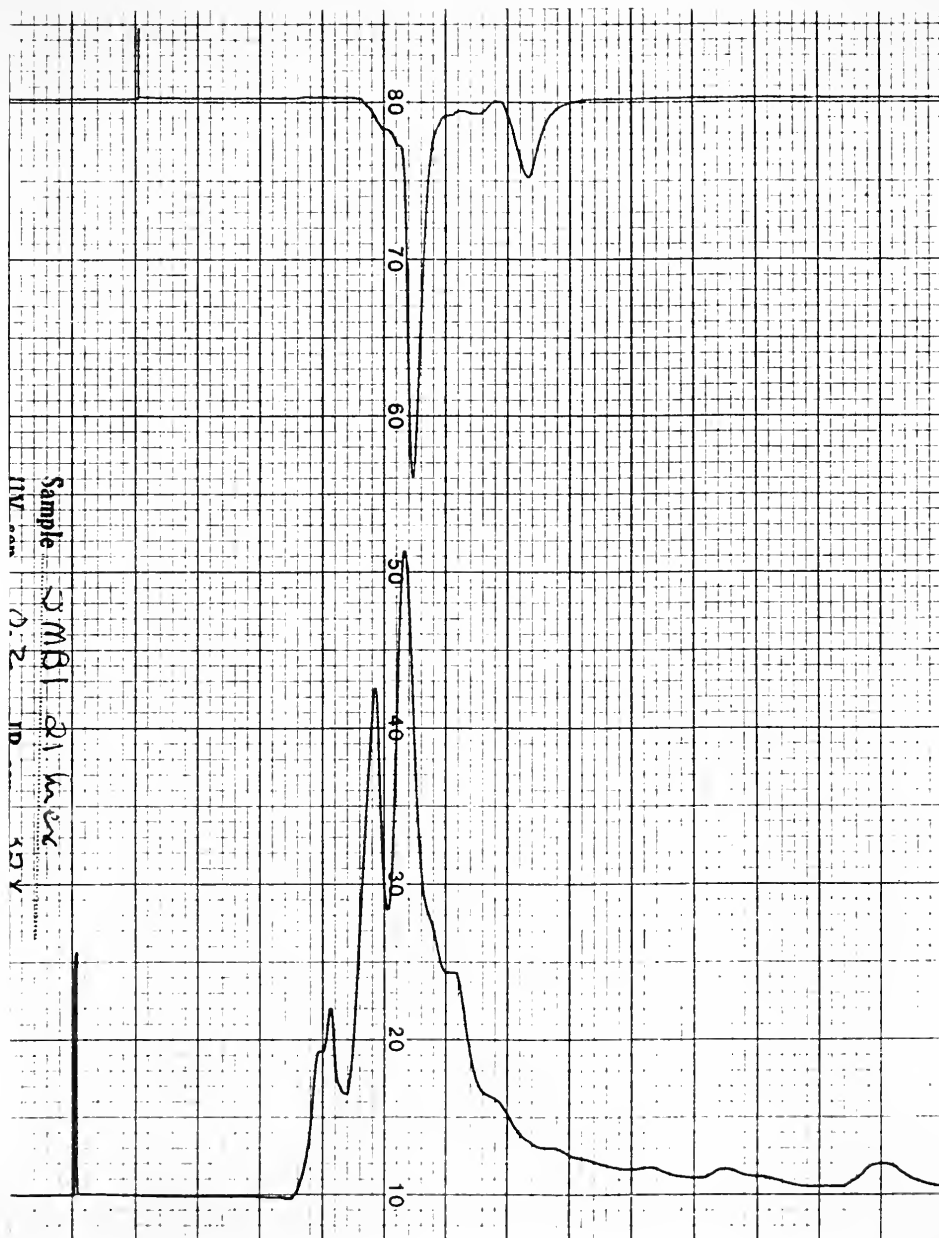


Fig. 19. Admixture K, 1X concentration.

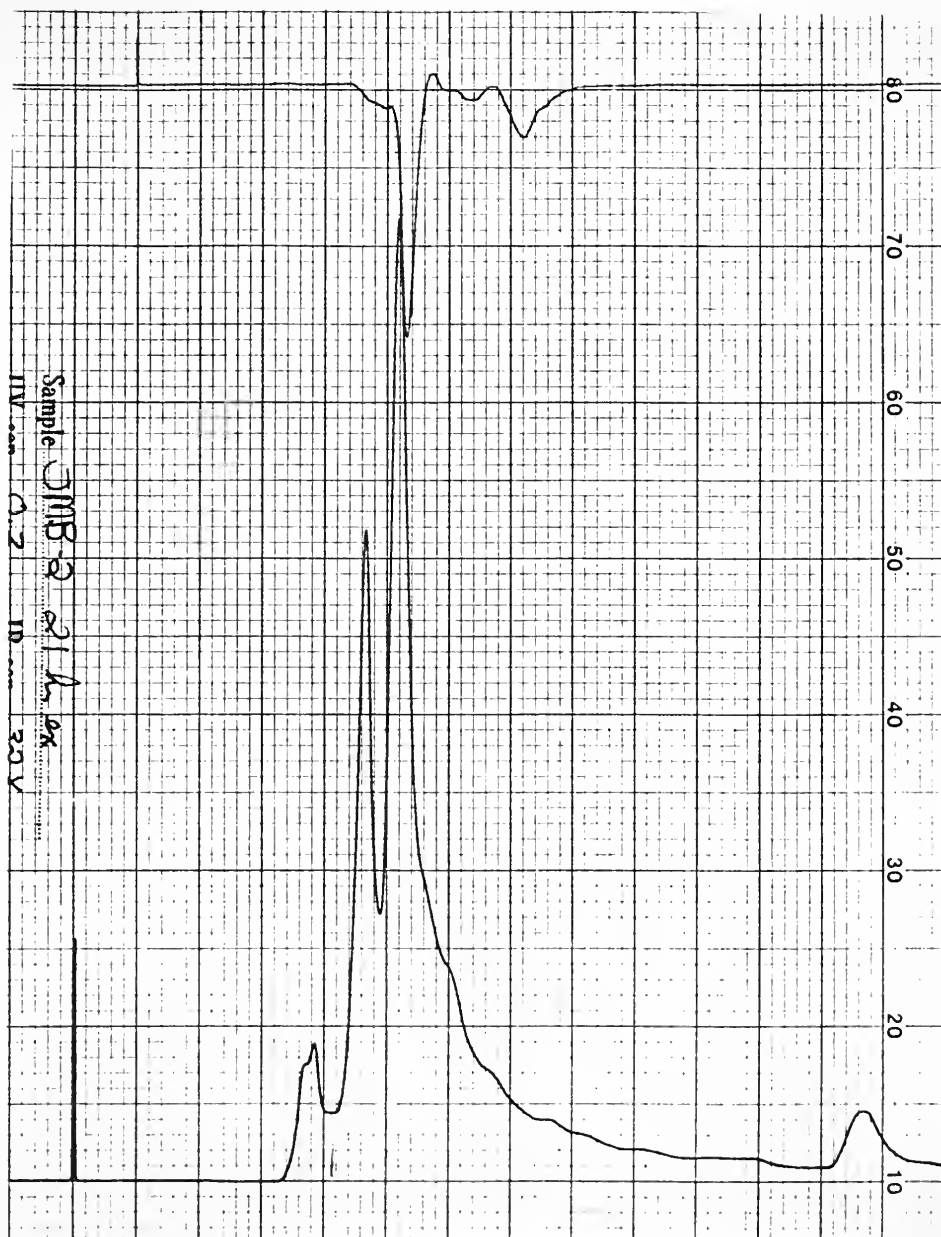


Fig. 20. Admixture K, 2X concentration.

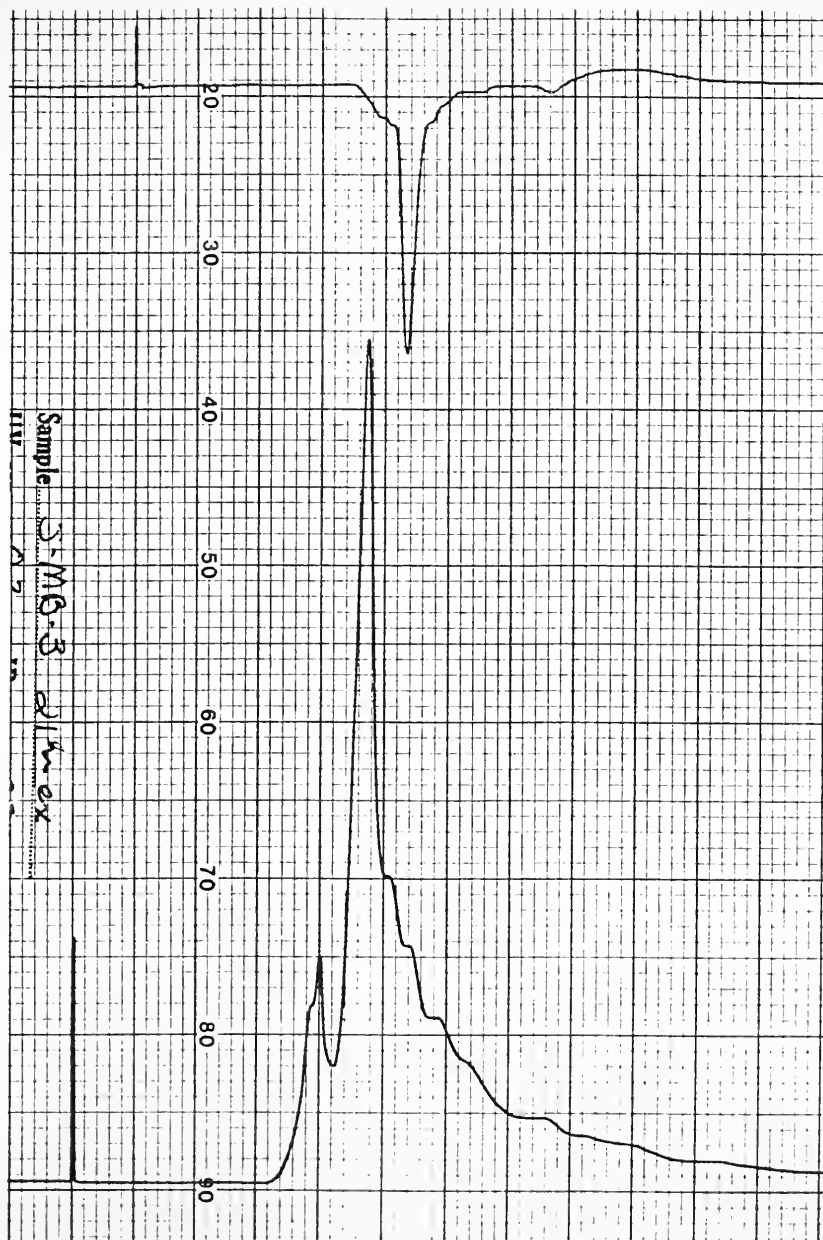


Fig. 21. Admixture K, 3X concentration.

